

Integration of first-principles methods and crystallographic database searches for new ferroelectrics: Strategies and explorations

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In this concept paper, the development of strategies for the integration of first-principles methods with crystallographic database mining for the discovery and design of novel ferroelectric materials is discussed, drawing on the results and experience derived from exploratory investigations on three different systems: (1) the double perovskite $\text{Sr}(\text{Sb}_{1/2}\text{Mn}_{1/2})\text{O}_3$ as a candidate semiconducting ferroelectric; (2) polar derivatives of schafarzikite MSb_2O_4 ; and (3) ferroelectric semiconductors with formula $\text{M}_2\text{P}_2(\text{S},\text{Se})_6$. A variety of avenues for further research and investigation are suggested, including automated structure type classification, low-symmetry improper ferroelectrics, and high-throughput first-principles searches for additional representatives of structural families with desirable functional properties.

INTRODUCTION

One of the central challenges in modern materials science is the discovery and design of functional materials that can be readily incorporated into a useful device with practical applications. The effectiveness of theoretical input into this process has been increasingly recognized [1, 2]. First principles prediction of the structure and properties of both real and as-yet hypothetical materials can play a valuable role in the screening of candidate materials for experimental investigation. The theoretical component of materials discovery and design can be further strengthened by the effective use of crystallographic database information to identify systems and structural families to be screened. Our hope, by effective use of the database in conjunction with first principles methods, is to enhance the value of our theoretical input to experimental collaborators, who are the essential contributors in any materials discovery/design effort, and thus to expedite and increase the chances of success of the overall process. However, effectively joining both database and first principles methods to develop systematic and efficient strategies requires experience through application to specific materials challenges, such as the search for new ferroelectric materials.

Ferroelectric materials are a class of functional materials which are particularly well suited to rational discovery and design approaches. A ferroelectric is an insulating material characterized by a electric polarization that is switchable by an applied electric field; this polarization generally arises from a polar structural distortion of a high-symmetry reference structure. An applied electric field can thus be used directly to manipulate the electric polarization of a ferroelectric, and thus also control any properties, including strain, magnetism, and optical response, that are coupled to the polarization. Well-established technological applications of ferroelectrics include nonvolatile information storage associated with the multiple polarization states [3], and transducers, exploiting the piezoelectric response of the polar crystal structure and polability of polycrystalline materials [4].

The optical and electronic properties of ferroelectrics offer further possibilities for technological application, with potential impact on electronics [5] and energy conversion and storage [6]. Of particular interest is the possibility of electric field control of optical and electronic properties via the switchable polarization. For example, in a doped ferroelectric semiconductor, the polar distortion can couple to the carriers and produce characteristic transport properties [7] including a switchable diode effect and a bulk photovoltaic effect, in which absorption of light by a piezoelectric material generates an asymmetric carrier distribution resulting in a net current [8]. These effects have been recently observed [9–12] in the ferroelectric perovskite oxide BiFeO_3 , the most-studied room-temperature multiferroic [13, 14].

Ferroelectric semiconductors, with bandgaps in or below the visible range, are therefore of particular interest. BiFeO_3 has received attention as it combines a high ferroelectric polarization with a semiconductive band gap of 2.7 eV. However, as shown in Figure 1, there are virtually no ferroelectric materials with both a high polarization and a lower band gap, as demonstrated by the empty space outlined by the red box. The challenge thus is to discover materials in this region.

One route to increasing the number of ferroelectric semiconductors is by band gap engineering: reducing the too-large gaps of known ferroelectric materials through compositional substitution or strain. Examples of the former include $\text{Pb}(\text{Ti}_{1-x}\text{Ni}_x)\text{O}_{3-x}$ [15, 16], $\text{Ba}(\text{Ti}_{1-x-y}\text{Ce}_x\text{Pd}_y)\text{O}_{3-y}$ [17] and PZN-type relaxors [18]. Recently it has been shown [19] that values of epitaxial strain that make SrTiO_3 ferroelectric also significantly reduce its band gap from the bulk value of 3.2 eV, greatly increasing its value as a photocatalyst.

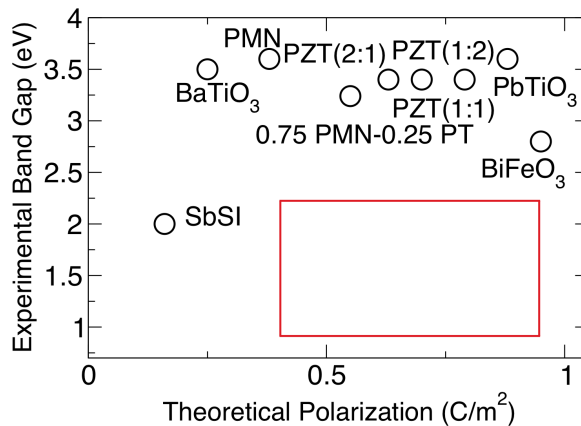


FIG. 1: The experimentally measured band gaps of a representative set of ferroelectric materials are plotted against the value of spontaneous polarization computed using first principles methods. The empty box outlined in red highlights the lack of ferroelectric materials with large polarization and smaller band gap comparable to the solar spectrum. From Ref. [15].

Another route to increasing the number of ferroelectric semiconductors is by inducing ferroelectricity in nonpolar semiconducting compounds with structures closely related to ferroelectrics. This can be done through changes in composition or epitaxial strain that either destabilize a polar mode, as in SrTiO_3 [20] and CaTiO_3 [21] under epitaxial strain, or destabilize one or more nonpolar modes that satisfy the symmetry conditions to produce a polarization, resulting in an improper ferroelectric material [22]. Examples of improper ferroelectrics include YMnO_3 , a layered structure in which a zone boundary mode induces a polarization [23, 24], and systems in which a polarization is induced by a trilinear coupling of polarization to two oxygen octahedron rotation modes: Ruddlesden-Popper phase $\text{Ca}_3(\text{Ti,Mn})_2\text{O}_7$ [25], the double perovskite $(\text{Na,L a})(\text{Mn,W})\text{O}_6$ [26], and $(\text{PbTiO}_3)_1/(\text{SrTiO}_3)_3$ superlattices [27].

While the two routes described above increase the number of semiconducting ferroelectrics by incremental modifications of familiar systems, there is also great interest in discovering novel ferroelectric compounds. To do this, we extend the range of the search beyond known ferroelectrics to all polar materials, because any polar structure type also can in principle have representatives that are ferroelectric. This requires that the energy of the polar distortion which relates the polar subgroup structure to the nonpolar supergroup structure be small in the sense that the corresponding energy barrier can be overcome by electric fields less than the breakdown field of the material. Thus in the space of polar structures, we target materials that have a low barrier to polarization switching as well as a low band gap.

The design of new ferroelectric materials can therefore draw on design principles for polar materials [28, 29]. For example, one design principle that has been considered is the combination of polar molecular units as counterions that promote arrangements in which the polar units align to produce a macroscopic polarization [30–32].

First, we focus on discovery of previously-unrecognized ferroelectrics among systems reported in the crystallographic literature, since this information is readily available in crystallographic databases such as the Inorganic Crystal Structural Database (ICSD) [33]. Analyses of polar oxides and sulfides have previously been carried out [34, 35]. Our search for new semiconducting ferroelectrics includes not only polar oxides and sulfides, but the full range of polar systems in the ICSD. In addition to a polar space group, we require a low energy difference from a high-symmetry reference structure, to promote switchability, and a low band gap. In earlier work, Abrahams has searched for previously-unrecognized ferroelectrics by combining the space group criterion with a structural criterion as a proxy for switchability [36–38]. Here, we similarly search for proximity to a high symmetry reference structure, and include the chemical requirement of inclusion of a main group element to promote the lower band gap. For individual compounds of interest, we supplement the results from the database with first principles calculations, obtaining not only structural information, but the band structure and the energy barrier to the high-symmetry reference structure needed to identify ferroelectric character in a system. Moreover, with recent advances in the speed and accuracy of first-principles methods, it has become practical to enhance and extend the information in the database by first principles calculations of the structure and properties of both real and hypothetical materials in a high-throughput mode [39–45], as exemplified by recent searches for high-performance piezoelectrics [42, 43, 45].

In the past two years, we have been developing the integration of database searches and first-principles methods to identify novel polar compounds with desirable properties, with a particular focus on semiconducting ferroelectrics. By attacking a series of pilot problems, we have explored a variety of strategies to develop useful search criteria and

efficiently search for materials realizations. In this concept paper, after a survey of the polar space groups and major polar structure types in the ICSD, we describe the results of three of these exploratory investigations, and discuss the lessons learned that have shaped our development of a systematic method [45–47].

METHODOLOGY

A wealth of information about naturally occurring crystal structures and the relationship between structure and composition is inherent in a comprehensive crystallographic database. Here, we use the ICSD [33], which contains 142,000 entries, with new entries being added at the rate of about 7,000 each year. The entry for a given system contains information about composition and the lattice type and parameters; additional information includes space group, occupied Wyckoff positions and structural parameters, refinement data such as thermal factors, warnings and comments, and structure type. Online searches can select for the number and/or type of distinct chemical elements in the compound, the space group, and a variety of other fields. So, for example, one can list all ternary compounds with a given space group, or all compounds with a given stoichiometry.

As large as the major crystallographic databases are, they are still incomplete in many ways. We use first principles total-energy and band structure calculations, equally feasible both for real and hypothetical structures, to complement the database information. First, prediction of the lowest energy structure is a standard application of first principles total-energy methods [48]. For a given compound in the database, we can compare the observed structure type with other likely candidate structure types, minimizing the total energy with respect to the structural parameters in each case. Comparison of the result for the lowest energy structure and its structural parameters with the experimental information in the database can confirm the latter or alternatively cast it into question for further investigation.

In addition, for a given compound in the database we can compute experimentally measurable physical properties that are not included, such as band gap, magnetization, electric polarization, phonon frequencies, dielectric constants, and piezoelectric coefficients. Finally, we can search for additional representatives of a structure type with desired properties by considering a large number of candidate compositions and calculating the structure, stability and relevant properties of the hypothetical compounds in a high-throughput study.

First principles calculations can be performed with a variety of widely available software packages. For the calculations described in this paper, we used ABINIT [49]. Optimized [50] norm-conserving [51] pseudopotentials were generated using the OPIUM code [52]. The k-grid for structural optimizations was at least $4 \times 4 \times 4$ [53]. Additional details for each case will be given below.

RESULTS

Survey of known polar systems

We begin by surveying all polar systems in ICSD, extending the previous surveys for polar oxide and sulfide materials [34, 35]. Of the 230 space groups, 68 are polar. The number of entries reported in these 68 space groups is 12,553, which is less than ten percent of the total number of entries in the database (142,000). Polar compounds can therefore be said to be relatively rare.

These polar entries can be sorted into six crystal lattice systems, each containing one or more crystal classes: hexagonal ($6mm$ and 6, with 2264 compounds representing 18.0% of the total), rhombohedral ($3mm$ and 3, with 2411 compounds at 19.2%), tetragonal ($4mm$ and 4 with 851 compounds, 6.8%), orthorhombic ($mm2$ with 4033 compounds, 32.1%), monoclinic (2 and m with 2534 compounds, 20.2%) and triclinic (1 with 460 compounds, 3.7%) entries. The most familiar ferroelectric materials are rhombohedral (LiNbO_3), hexagonal (YMnO_3) and tetragonal (PbTiO_3 and BaTiO_3), yet there are twice as many polar orthorhombic entries as there are either rhombohedral or hexagonal, and four times as many polar orthorhombic entries than there are tetragonal entries. This result indicates that searches among orthorhombic compounds for previously-unrecognized ferroelectrics might be particularly rewarding, and indeed ferroelectricity might be favored by the lower symmetry.

Next, we turn to closer examination of the composition and structure of individual polar systems. Each entry can be characterized as elemental (0.3%), binary (14.3%), ternary (29.9%), quaternary (30.4%) or containing 5+ (25.1%) distinct chemical elements; this breakdown is given for each polar space group in Tables I and II. We divide the breakdown of entries into two tables to emphasize the distinction between crystal classes that contain common ferroelectrics (Table I: hexagonal, rhombohedral, tetragonal) and crystal classes in which few ferroelectrics are well known (Table II: orthorhombic, monoclinic, triclinic).

Crystal Class	Space Group	Total Entries	1	2	3	4	5+	Most Common Structure Types	Unassigned
6mm	186	1327	6	374	551	248	148	LiGaGe (139), ZnS (445)	118 (8.9%)
	185	169	0	32	67	52	18	LuMnO ₃ (54), LaF ₃ (25)	46 (27.2%)
	184	15	0	0	5	2	8	zeolite (9)	5 (33.3%)
	183	19	0	1	7	9	2	none	19 (100%)
6	173	681	0	29	125	304	223	Apatite (39), La ₃ CuSiS ₇ (177)	145 (21.3%)
	172	1	0	0	0	1	0	none	1 (100%)
	171	5	0	3	0	1	1	none	5 (100%)
	170	13	0	1	0	7	5	Ba(NO ₂) ₂ *2H ₂ O (5)	7 (53.9%)
	169	33	0	6	9	6	12	Al ₂ S ₃ (11)	16 (48.5%)
	168	1	0	0	0	1	0	none	0 (0.0%)
3mm	161	587	0	22	212	221	132	LiNbO ₃ (287), whitlockite (61)	118 (20.1%)
	160	798	0	276	215	102	205	ZnS (123), FeBiO ₃ (79)	216 (27.1%)
	159	168	2	27	22	57	60	Si ₃ N ₄ (18)	80 (47.6%)
	158	22	0	5	3	7	7	none	22 (100%)
	157	72	0	3	28	26	15	Mg ₃ Si ₂ O ₅ (OH) (19)	30 (41.7%)
	156	347	0	259	29	53	6	CdI ₂ (137)	116 (33.4%)
3	146	214	1	12	76	76	49	Ni ₃ TeO ₆ (12)	131 (61.2%)
	145	22	0	1	7	6	8	RbNO ₃ (2)	19 (86.4%)
	144	82	0	16	23	32	11	RbNO ₃ (16)	42 (51.2%)
	143	99	1	13	33	21	31	NiTi (6)	86 (86.9%)
4mm	110	51	0	4	28	10	9	Li ₂ B ₄ O ₇ (22)	11 (21.6%)
	109	50	0	11	30	6	3	LaPtSi (16)	19 (38.0%)
	108	29	0	1	21	5	2	Pb ₅ Cr ₃ F ₁₉ (4)	25 (86.2%)
	107	121	0	13	69	17	22	BaNiSn ₃ (43)	44 (36.4%)
	106	5	0	0	2	3	0	none	5 (100%)
	105	5	0	0	4	1	0	none	5 (100%)
	104	9	0	0	5	0	4	Tl ₄ HgI ₆ (4)	5 (55.6%)
	103	8	0	6	2	0	0	NbTe ₄ (7)	1 (12.5%)
	102	23	4	6	5	4	4	Al ₂ Gd ₃ (4)	12 (52.2%)
	101	3	0	0	3	0	0	none	3 (100%)
	100	97	0	1	16	57	23	BSN (21), Ba ₂ TiOSi ₂ O ₇ (23)	20 (20.6%)
	99	299	0	6	104	82	107	PbTiO ₃ (210), PbVO ₃ (12)	32 (10.7%)
4	80	16	0	3	6	5	2	none	16 (100%)
	79	42	0	5	20	7	10	U ₃ Al ₂ Si ₃ (6)	29 (69.1%)
	78	12	1	0	6	1	4	none	12 (100%)
	77	10	0	4	4	2	0	H ₂ S (3)	7 (70.0%)
	76	48	2	5	22	4	15	Ca ₂ P ₂ O ₇ (16)	23 (47.9%)
	75	23	0	7	4	6	6	K ₄ CuV ₅ O ₁₅ Cl (4)	19 (82.6%)

TABLE I: For each polar space group of hexagonal, rhombohedral and tetragonal symmetry, arranged according to crystal class, we record the total number of entries, the breakdown into entries containing 1, 2, 3, 4 or 5+ distinct chemical elements, the most common structure types with the corresponding number of representatives, and the number of entries for which no structure type is reported, also expressed as a percentage of the total number of entries for the given space group.

It is intriguing to notice that there are reports in ICSD of elemental systems with polar structures (the proportion 0.3%, given above, corresponds to 40 entries). On closer inspection, we find most of these to be misassigned, with the given atomic positions giving a higher-symmetry nonpolar structure within experimental error. However, there are a few that appear to be truly polar, including Po with a reported monoclinic $C2(5)$ structure, and these warrant further investigation. Structures of systems with two or more distinct chemical elements can be recognized either as a solid solution which can be related to a simpler structure with fewer distinct chemical elements, or as an inherently more complex structure. In particular, many of the entries that have 5+ distinct chemical elements have fractional occupation of Wyckoff positions, indicative of a solid solution.

A more detailed classification of polar structures can be obtained by grouping entries according to structure type.

Crystal Class	Space Group	Total Entries	1	2	3	4	5+	Most Common Structure Types	Unassigned
<i>mm2</i>	46	179	0	4	52	52	71	Ca ₂ AlFeO ₅ (79), ErSr ₂ GaCu ₂ O ₇ (27)	53 (29.6%)
	45	33	0	0	15	8	10	Ca ₁₁ InSb ₉ (5), Sr ₄ Fe ₆ O ₁₃ (15)	17 (51.5%)
	44	153	0	25	78	31	19	NaNO ₂ (13)	74 (48.4%)
	43	287	0	43	44	87	113	Natrolite (61)	111 (38.7%)
	42	69	1	23	21	16	8	NbS ₂ (10)	47 (68.1%)
	41	117	0	18	24	54	21	Bi ₄ Ti ₃ O ₁₂ (15)	71 (60.7%)
	40	107	0	15	16	58	18	NaCu ₂ NbS ₄ (14)	55 (51.4%)
	39	42	0	14	15	7	6	LaS (5)	31 (73.8%)
	38	186	2	51	86	37	10	CeNiC ₂ (29)	108 (58.1%)
	37	22	0	0	6	4	12	none	22 (100%)
	36	691	1	65	268	214	143	Bi ₃ TiNbO ₉ (87)	249 (36.0%)
	35	41	0	1	6	16	18	none	41 (100%)
	34	55	0	5	8	25	17	Ca ₂ B ₅ O ₉ Br (12)	35 (63.6%)
	33	1087	2	68	300	377	340	Cu ₂ Sc ₂ O ₅ (18), NaFeO ₂ (56)	258 (23.7%)
	32	48	0	5	15	10	18	K _{1-x} FeF ₃ (4)	33 (68.8%)
	31	376	0	16	136	114	110	Cu ₃ AsS ₄ (56)	157 (41.8%)
	30	20	0	2	3	5	9	Fe ₃ (PO ₄) ₂ *H ₂ O	19 (95.0%)
	29	305	1	11	83	124	86	boracite (16)	184 (60.3%)
	28	30	0	6	12	2	10	AuTe ₂ (5)	20 (66.7%)
	27	5	0	1	3	1	0	V ₄ H ₃ (1)	4 (80.0%)
	26	133	0	9	37	59	28	NaNbO ₃ (5)	88 (66.2%)
	25	47	0	17	12	12	6	GaAs (7)	29 (61.7%)
<i>m</i>	9	621	0	40	159	215	207	Pb(Ti,Zr)O ₃ (14)	339 (54.6%)
	8	350	0	30	103	116	101	Ca ₅ (BO ₃) ₃ F (17), Pb ₂ FeNbO ₆ (48)	199 (56.9%)
	7	307	0	51	68	108	80	WO ₃ (32)	189 (61.6%)
	6	59	0	7	13	22	17	PMN-PT and (Na,K)NbO ₃ (17)	42 (71.2%)
2	5	430	1	30	123	152	124	many	292 (67.9%)
	4	722	10	35	151	282	244	many	415 (57.5%)
	3	45	2	4	11	13	15	none	45 (100%)
1	1	460	6	52	118	150	134	many	324 (70.4%)

TABLE II: For each polar space group of orthorhombic, monoclinic, and triclinic symmetry, arranged according to crystal class, we record the total number of entries, the breakdown into entries containing 1, 2, 3, 4 or 5+ distinct chemical elements, the most common structure types with the corresponding number of representatives, and the number of entries for which no structure type is reported, also expressed as a percentage of the total number of entries for the given space group. The term “many” appearing under most common structure type means that no one or two structure types have more representatives than a number of others.

Entries in ICSD report the assignment from the original article (59.7% of entries), though in many cases (40.3%) none is made. In Tables I and II, for each space group we list the most commonly reported structure types and the number of representative entries for each of these structure types. There are two space groups strongly dominated by common structure types: hexagonal space group 186 and tetragonal space group 99. In space group 186 the two most common structure types are ZnS with 445 entries and LiGaGe with 139 entries, which represent 44.0% of the 1327 total entries. In space group 99 the three most common structure types, PbTiO₃, (210 entries) KNbO₃ (17 entries) and PbVO₃ (12 entries), are all related to the perovskite structure and account for 79.3% of the 299 entries. At the other extreme, there are 13 space groups in which all entries have no reported structure type: 183, 172, 171, 168, 158, 106, 105, 101, 80, 78, 37, 35 and 3; however the total number of entries in these groups is only 196, or 1.6% of the total number of all polar entries.

While a systematic classification system for the assignment of inorganic structure type has been established [54], it seems that these conventions are not always followed in the literature, and thus not in the ICSD. The case of tetragonal space group 99 illustrates the problem of structure type nomenclature: the similarity of the PbTiO₃ and KNbO₃ structures suggests that, following the guidelines of Ref. [54], these should be combined and regarded as a single structure type. An automated classification method based on the structural information in ICSD would reduce or even eliminate such problems, and could also assign missing structure types, especially in cases where the system is chemically different from other representatives and the structural relationship was not recognized by the authors of

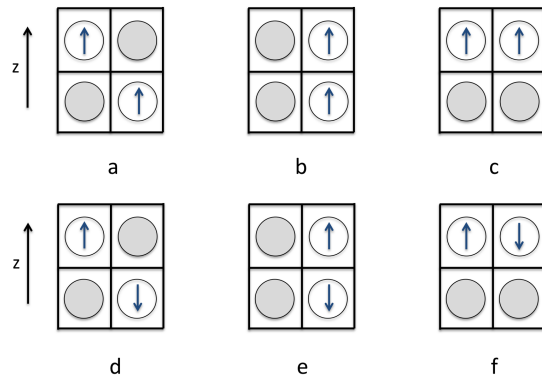


FIG. 2: Sketches of the magnetic and cation ordering for the six $\text{Sr}(\text{Sb}_{1/2}\text{Mn}_{1/2})\text{O}_3$ configurations considered. a through c are FM and d through f are AFM ordered rocksalt, pillars and layers, respectively. The boxes represent perovskite unit cells, Sb are shown as shaded circles, and the spin state of each Mn (open circles) is shown with an arrow as spin up or down.

the original paper. This would make the classification by structure type much more useful, and in particular would make it possible to easily identify unusual or exotic compounds with a given structure type of interest.

For the discovery of ferroelectric materials, these results suggest two complementary strategies. The first is to search the database to identify previously-overlooked systems in structure types of known ferroelectrics and use first-principles methods to screen these systems for exceptional properties. The second is to identify additional structure types for which no ferroelectrics have been previously reported, but for which ferroelectricity could be established either in known representatives through further experimental investigation, or in additional representatives identified through a first-principles high-throughput study. We develop both strategies in the three exploratory investigations discussed next.

$\text{Sr}(\text{Sb}_{1/2}\text{Mn}_{1/2})\text{O}_3$: A semiconducting ferroelectric?

In our first exploratory investigation, we show how first principles calculations can be used to complement a database search for previously-overlooked ferroelectric oxides. In this case, the database search was performed not by us, but previously by Abrahams [37] as part of a large-scale research program to identify previously-overlooked ferroelectric materials in the ICSD. This search resulted in the identification of a number of candidate ferroelectrics, including the double perovskite $\text{Sr}(\text{Sb}_{1/2}\text{Mn}_{1/2})\text{O}_3$ [55]; this system was of particular interest to us because one-half of the octahedral units contain a main group element (Sb) which could promote a lower band gap, making the system a ferroelectric semiconductor. In addition, the presence of the transition metal Mn could lead to magnetic and multiferroic behavior. However, since this search was performed in 1996, there have been at least five additional reports of the same system in various, mostly nonpolar, tetragonal space groups, calling the ferroelectric character of the system into question. This suggests that it would be illuminating to study the structural energetics of this system from first principles.

The original report [56] assigns room temperature $\text{Sr}(\text{Sb}_{1/2}\text{Mn}_{1/2})\text{O}_3$ to polar space group $I4mm$ (107) with full rocksalt ordering for the Sb and Mn on the B site. The ICSD includes several later entries for this system, reporting different tetragonal space groups including nonpolar $I4/mcm$ (140, no cation order) [57], and nonpolar $I4/m$ (87, partial rocksalt cation ordering) [58–60]. A value for the band gap of 0.50(2) eV was extracted from the Arrhenius behavior of the conductivity in Ref. [55] (in which the space group was reported to be polar $I4mm$, consistent with Ref. [56]).

To clarify the question of space group assignment and polar character of $\text{Sr}(\text{Sb}_{1/2}\text{Mn}_{1/2})\text{O}_3$, we begin by computing total energies and optimized structural parameters for various choices of magnetic and cation ordering. We consider three types of cation ordering (rocksalt, 2D checkerboard of Mn and Sb pillars, and alternating layers of Mn and Sb) and two types of magnetic ordering on the Mn sublattice, ferromagnetic (FM) and antiferromagnetic (AFM), as shown in Figure 2. All six combinations can be accommodated by a $\sqrt{2} \times \sqrt{2} \times 2$ supercell. The total energy calculations and structural relaxations are performed with a starting structure with atomic positions and cell parameters taken from Ref. [56], as given in Table 1 of Ref. [55], combined with an additional oxygen octahedron rotation around z , alternating from plane to plane, taken from Ref. [57]. As will be further discussed below, this choice guarantees that

	a	c	ΔE	Γ_4^-	R_5^+	X_3^-	M_2^+	M_4^+	R_2^-	R_3^-	R_5^-
Expt. ($I4mm$)	5.526	8.039	-	0.346	0.020	0	0	0	0.160	0.054	0
Expt. ($I4/m$)	5.533	8.085	-	0	0	0	0	0	0.003	0.093	0.385
Expt ($I4/mcm$) rocksalt	5.556	8.055	-	0	0	0	0	0	0	0	0.332
FM ($I4/m$)	5.548	8.135	0.12	0	0	0	0	0	0.095	0.029	0.614
AFM ($I4/m$)	5.459	8.299	0.13	0	0	0	0	0	0.108	0.048	0.702
pillars											
FM ($P4/mcc$)	5.536	8.212	0.41	0	0	0	0	0.066	0	0	0.630
AFM ($P4/m$)	5.539	8.133	0.50	0	0	0.023	0.005	0.083	0.022	0.022	0.636
layers											
FM ($P4/mbm$)	5.459	8.208	0	0	0	0.274	0.426	0	0	0	0.492
AFM ($P4/mbm$)	5.520	8.190	0.08	0	0	0.297	0.442	0	0	0	0.520

TABLE III: Structural data for $\text{Sr}(\text{Mn}_{1/2}\text{Sb}_{1/2})\text{O}_3$ from experimental reports and from first principles calculations for the six ordered configurations considered. Lattice constants a and c are in Å. ΔE is the computed energy per 10-atom formula unit, in eV, relative to the minimum energy FM layered configuration. The remaining columns give the amplitude of each normal mode distortion needed to specify the atomic positions, as discussed in the text.

the structure can relax to any of the experimentally observed structure types. Examination of the relaxed structure obtained from this starting point will reveal if any symmetries are broken beyond those determined by the cation and magnetic ordering.

To describe the relaxed structures in a way that allows us directly to compare all six magnetic and cation orderings, we use the amplitudes of symmetrized displacement patterns defined with respect to the high-symmetry reference structure where the atoms are at the ideal cubic perovskite positions and all B site cations are treated as symmetry equivalent. For a given relaxed structure, we obtain the amplitudes of the contributing patterns using the program ISODISTORT, which establishes the conventions for the perovskite modes [61].

The cation and magnetic orderings of the ordered supercells break symmetries that induce atomic displacements of corresponding symmetry types, as follows: for the rocksalt ordering, the breathing pattern R_2^- , in which the surrounding oxygens move in towards one B cation and out from the other; for pillar ordering, the xy -plane breathing pattern M_4^+ , in which the surrounding equatorial oxygens move in towards one B cation pillar and out from the other; and for the alternating layers, the z -breathing pattern X_3^- , in which apical oxygens move towards one B cation layer and away from the other. Note that in the absence of spin-orbit coupling, the crystallographic symmetry of the FM and AFM structures is the same.

The symmetrized displacement patterns that comprise the starting structure described earlier are Γ_4^- (a polar mode with displacements along z), the breathing mode R_2^- , the Jahn-Teller mode R_3^- (where equatorial oxygens move in towards and apical oxygens move away from one B cation) and the oxygen octahedron rotation mode R_5^- , with rotations around z alternating from plane to plane. For the layer and pillar supercells, cation ordering breaks additional symmetries as described above. In the course of relaxation, the distortion patterns that do not lower the energy will relax to zero, restoring the corresponding symmetry.

The results are presented in Table III. It is immediately clear that the oxygen-octahedron rotation R_5^- is a strong instability independent of cation and magnetic ordering, while the ferroelectric distortion does not appear in any of the ordered supercells. To be more specific, for rocksalt ordering, both FM and AFM systems relax to a tetragonal structure which combines the R_2^- breathing mode driven by the cation ordering with oxygen octahedron rotations corresponding to the R_5^- mode, which appears to be the driving instability, and a small amplitude for the R_3^- Jahn-Teller distortion that then appears without additional symmetry breaking; the Γ_4^- mode introduced by the starting positions relaxes to zero. This structure has the cation ordered $I4/m$ space group (87) identified in several experimental investigations [59, 60]. Similarly, for layered cation ordering, both systems relax to a tetragonal structure which combines the X_3^- breathing mode driven by the cation ordering with oxygen octahedron rotations generated by a combination of the R_5^- and M_2^+ modes, which produce rotations by different angles in the Sb and Mn layers. Finally, for the pillar ordering, the FM system relaxes to a tetragonal structure which combines the M_4^+ breathing mode driven by the cation ordering with oxygen octahedron rotations corresponding to the R_5^- mode. However, the AFM system has a small symmetry-breaking instability relative to the higher-symmetry structure imposed by the cation ordering and octahedron rotation mode alone, as confirmed by comparison of the total energy of the given structure with that of the optimized higher-symmetry structure. This is reminiscent of the spin-phonon coupling previously studied in other perovskite oxides, including EuTiO_3 [1] and SrMnO_3 [62], in which a change in magnetic

order can destabilize a phonon and lead to a symmetry-lowering distortion.

Our calculated ground state structure is the FM ordered alternating $\text{Sb}^{5+}/\text{Mn}^{3+}$ layered configuration. This ordering differs from that observed experimentally (rocksalt or partial rocksalt), and is further surprising in that it appears electrostatically unfavorable. However, its energy could be low due to the size mismatch between the two B-sites: (Sb^{5+} is 0.60 Å and Mn^{3+} is 0.65 Å) and correspondingly large relaxations, and it should be noted that the observed ordering, when present, reflects the synthetic conditions at high temperature rather than the ground state. Both rocksalt structures are roughly 0.12 eV per 5-atom formula unit higher in energy than the ground state, with the energy difference between FM and AFM very small (5 meV), while the pillar structures are much higher in energy. It is difficult to compare the predicted magnetic ordering with experiments; the reported ordering is a spin glass magnetic order and likely is related at least in part to the cation disorder.

For the six configurations, we computed the electronic band structure and found that all are metallic. When the band structure is recomputed with LDA+ U with values of $U > 3$ eV, a band gap is opened in the minority-spin channel, but not in the majority-spin channel, yielding a spin-polarized half-metal.

From this analysis, we conclude that $\text{Sr}(\text{Sb}_{1/2}\text{Mn}_{1/2})\text{O}_3$ is, in fact, neither semiconducting nor ferroelectric as proposed in Ref. [55], but has a nonpolar structure, as reported in subsequent papers for both disordered and partially ordered cases. This negative result, though disappointing when considered in the framework of the discovery of new ferroelectric materials, does illustrate the value of including first principles results in evaluating structural data.

Schafarzikite: $M\text{Sb}_2\text{O}_4$ ($M=\text{Mn, Fe, Ni, Zn}$)

In our second exploratory investigation, we consider the schafarzikites, a family of complex oxides reported with a nonpolar structure. We choose this structure because it contains magnetic elements within oxygen octahedra, that, unlike the conventional perovskite, are edge-sharing. In addition, the Sb are not within the octahedra, as in the previous example, but part of a chain that cross-links the octahedra. In this way, we have two cations of interest in two chemically different environments. We use first principles results to investigate whether the ground state structure of one or more compounds in this family might in fact be in a lower-symmetry polar space group. This could be the case if the reported nonpolar structure is either the result of a temperature-driven phase transition or simply a misassignment to a higher-symmetry space group. The latter possibility was pointed out to us by Prof. J. F. Scott of the University of Cambridge [63], based on the crystallographic practice of assigning a structure to the highest-symmetry space group consistent with the structural data. This suggests that some, perhaps many, polar compounds might be misreported in the database with higher (nonpolar) space groups.

The question of whether known nonpolar structure families could have representatives with polar instabilities has proved to be perennially fascinating, especially with regard to spinels and pyrochlores [64–66]. To choose a distinct nonpolar structure type for the present study, we searched ICSD for ternary antimony oxides, the main group element Sb being, as in the previous section, selected to promote a lower band gap in the hope of discovering new ferroelectric semiconductors. From these, we chose to investigate schafarzikites, whose edge-sharing oxygen octahedron chains aligned along a single direction might allow a polar distortion along the chain.

The structure of the schafarzikite family $M\text{Sb}_2\text{O}_4$ is shown in Figure 3. It has chains of edge-sharing M -centered octahedra, crosslinked by chains of Sb ions in trigonal pyramidal coordination with three oxygen atoms from the octahedral chains and its own lone pair. For $M=\text{Fe}$, A -type antiferromagnetism (anti-aligned along chains, aligned within the ab plane) is observed with $T_N = 45$ K. An interesting possibility has been raised [67] that doping on the Sb site could functionalize the material by controlling the electronic state of the transition metal cation, and hence its electrical and magnetic properties. This, in turn, could couple to polar instabilities, producing a multifunctional material.

Known representatives of the schafarzikite family have tetragonal space group 135 ($P4_2/mbc$), in the Pb_3O_4 structure type. ICSD contains entries in this structure type for compounds that contain Mn, Fe, Ni, and Zn, all of which are formally 2^+ cations. Zn^{2+} is not magnetic, but Mn, Fe and Ni should have magnetic interactions. For these compounds, we study FM and three types of AFM order: AFM alignment along the c chains and FM interchain in the ab plane (A type, magnetic group 28: $4'/m'm'm'$), FM alignment along the c chains and AFM interchain in the ab plane (C type, magnetic group 27: $4'/mmm'$), and AFM alignment along the c chains and AFM interchain in the ab plane (G type, magnetic group 25: $4'/m'm'm'$). Results of the structural relaxations are shown in Table IV.

From Table IV, it can be seen that the first principles results for the magnetic representatives are not in good agreement with available experimental data. The c/a ratio is overestimated and for $M=\text{Fe}$, our DFT results show zero band gap and a different magnetic ground state than that reported in Ref. [67]. This suggests that at the least, a DFT+ U calculation would be needed for an accurate description, and highlights the importance of choosing an

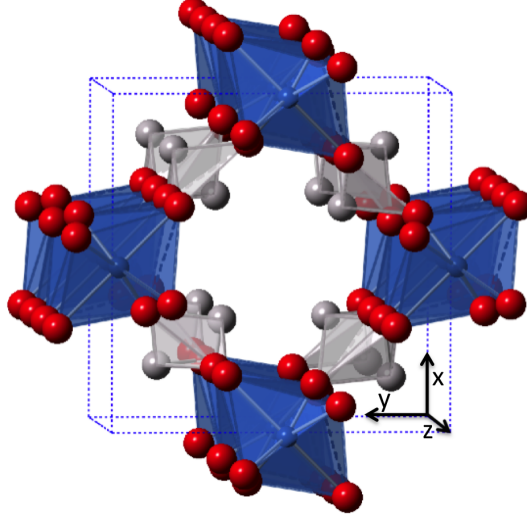


FIG. 3: The MSb_2O_4 schafarzikite structure contains chains of corner-sharing oxygen octahedra (blue) that are cross-linked by SbO_3 units (gray).

	a	c	E_{gap}	μ	ΔE
Mn					
FM	8.533 (-1.9%)	6.125 (+2.4%)	0.27	4.98	0.251
A	8.546 (-1.7%)	6.050 (+1.1%)	0.45	0	0
C	8.531 (-1.9%)	6.099 (+2.0%)	0.29	0	0.101
G	8.568 (-1.5%)	6.044 (+1.0%)	0.27	0	0.114
Fe					
FM	8.273 (-3.7%)	6.015 (+1.7%)	0	4.62	0.054
A	8.281 (-3.6%)	6.021 (+1.8%)	0	0	0.265
C	8.268 (-3.7%)	6.011 (+1.7%)	0	0	0
G	8.288 (-3.5%)	6.027 (+1.9%)	0	0	0.264
Ni					
FM	8.293 (-0.9%)	6.031 (+2.1%)	0.23	4.08	0.106
A	8.288 (-1.0%)	6.027 (+2.0%)	1.05	0	0.015
C	8.280 (-1.1%)	6.021 (+1.9%)	0.93	0	0
G	8.293 (-0.9%)	6.030 (+2.1%)	0.23	0	0.154
Zn					
-	8.487 (-0.5%)	5.873 (-1.16%)	1.92	0	0

TABLE IV: First-principles lattice constants for the four schafarzikite compounds MSb_2O_4 ($M = \text{Mn, Fe, Ni, Zn}$) are reported in Å, with error relative to experimental value in parentheses. The calculated band gap is given in eV. For the magnetic compounds ($M = \text{Mn, Fe, Ni}$), results are given for four different magnetic orderings: ferromagnetic (FM) and three different antiferromagnetic orderings described in the text (A type, C type and G type); for the FM configuration, the magnetic moment per M is given in μ_B .

appropriate functional in high-throughput first-principles studies. However, for non-magnetic $ZnSb_2O_4$ we find good agreement with experimental lattice constants and structural parameters [68].

Now, we investigate whether the ground state structure of $ZnSb_2O_4$ might in fact be in a lower-symmetry polar space group. We consider the polar structures which are related to the high-symmetry nonpolar $P4_2/mbc$ structure by freezing in a single normal mode; these are the most relevant in the search for new ferroelectrics. The modes that generate polar structures in this way can be identified through symmetry analysis, for which we use the software package ISOTROPY [69]. More specifically, we list the normal modes at the high-symmetry wavevectors $\Gamma(0,0,0)$, $X(\frac{\pi}{a},0,0)$ and $Z(0,0,\frac{\pi}{c})$. We consider the structure obtained by freezing in a single given mode, find the resulting space group and check to see if it is one of the 68 polar groups. First principles total-energy calculations are then performed to relax each of these polar structures to determine whether the polar distortion lowers the energy. This approach is much more computationally efficient than the alternative of calculating the full phonon dispersion and

checking the symmetry character of the unstable branches, because the symmetry analysis targets only the modes of interest.

Application of this symmetry analysis to the schafarzikite structure yields the following list of candidate polar structures. Zone center modes Γ_3^- and Γ_5^- decrease symmetry to $P4_2bc$ (106) and $Ama2$ (40), $Pmc2_1$ (26) or Pm (6) respectively; zone boundary modes $Z1$, $Z2$, $X1$ and $X2$ decrease symmetry to $Pba2$ (32), $Pnn2$ (34), $Pca2_1$ (29) (or Pc (7)), and $Pmc2_1$ (26) (or Pm (6)) respectively.

Using first principles calculations, we investigated the stability of the polar $P4_2bc$ (106) structure, obtained by a zone center Γ_3^- mode, which induces polarization along c . We froze in a Γ_3^- distortion, breaking the symmetry to $P4_2bc$, and performed a structural relaxation. For $M=Zn$, we found that symmetry breaking distortions to this polar space group relax back to the original non-polar structure, confirming the correct assignment of the nonpolar space group in this case. Analogous calculations for our ground state structures for $M=Fe$ and Ni yielded the same result, though as noted above, calculations with DFT+ U would be necessary for a definitive result for these two systems.

The zone boundary modes that produce polar space groups in this structure are especially interesting, as an instability to one of these modes would make the system an improper ferroelectric. It is extremely unlikely, though, that this would yield a bulk structure for the compounds considered, as the cell doubling would be readily manifest in any structural determination. However, it might be possible to induce an instability either in the zone center polar modes or in one of the zone boundary modes by perturbations such as compositional substitution or epitaxial strain, and we believe this could reward further investigation.

The fact that it turns out that the particular system chosen for this example was in all likelihood correctly assigned as nonpolar in the original literature, amounting to a negative result in the present search for new ferroelectrics, does not invalidate the initial hypothesis that some, perhaps many, polar compounds have been misreported as nonpolar. Systematic consideration of a number of nonpolar structure types would be needed to establish how prevalent such misassignment or low-temperature phase transitions might be, and to develop principles to identify nonpolar structure types with a tendency to polar instabilities. However, the identification of routes to improper ferroelectricity in this relatively low-symmetry nonpolar structure is intriguing, and further investigation in other low-symmetry nonpolar structure families seems warranted.

$M_2P_2(S,Se)_6$ chalcogenides

In our final exploratory investigation, we use a known semiconducting ferroelectric chalcogenide as a starting point for a database search which identifies both additional representatives in the family that could show a ferroelectric transition and polarization, and a different family of compounds with the same stoichiometry that also shows previously reported, though largely overlooked, indications of ferroelectricity.

Materials which contain chalcogenide anions, such as S, Se and Te, have a lower band gap than their O analogues, because the larger, more polarizable chalcogenide anions form bonds to metals that are more covalent and less ionic in nature than O. This principle has been of great interest in the field of solar energy harvesting, as materials based on the chalcopyrite structure ($CuFeS_2$) such as $Cu(In_{1-x}Ga_x)Se_2$ (CIGS), can be readily processed as films and nanostructures. This principle has also stimulated interest in perovskite sulfides such as $BaZrS_3$, which has a theoretical bandgap of 1.7 eV, lower than that calculated for the corresponding oxide $BaZrO_3$ (3.9 eV) [70]. However, the chalcopyrites and known perovskite sulfides have nonpolar structures.

A paraelectric-ferroelectric transition has been identified in the semiconducting chalcogenides $M_2P_2X_6$ ($M=Sn, Pb$ and $X=S, Se$), and well studied by a variety of methods [71–76]. Further interest was stimulated by the observation of a photovoltaic effect in $Sn_2P_2S_6$ crystals [77]. First principles studies of $Sn_2P_2Se_6$ show $E_{gap} \approx 1$ eV, and P is 0.15 C/m² [78]. The structure of these compounds is shown in Figure 4. Layers of M ions alternate with layers of P_2X_6 units, in which each P is tetrahedrally bound to four chalcogenide anions. The polarization arises from asymmetric displacements of the M -sites (Sn^{2+} or Pb^{2+}), both of which contain stereochemically active lone pairs. The displacement of the M -sites causes a decrease in symmetry from nonpolar space group $P2_1/c$ (14) to polar space group Pc (7).

To identify other members of the $M_2P_2X_6$ family, we searched ICSD for 3-element compounds $MP(S,Se)$ that have 1:1:3 stoichiometry and include P and either S or Se . Most of the entries have nonpolar structures. In space group $P2_1/c$ (14) there are six selenides ($M=Sn, Pb, Ca, Sr, Ba$ and Eu) and one sulfide, $Sn_2P_2S_6$, which all have the paraelectric structure discussed above. In space group $P3_121$ (152) there are two selenides ($M=K, Rb$), in $R\bar{3}$ (148) there are four selenides ($M=Mg, Zn, Fe, Mn$), in $Immm$ (71) there are four sulfides ($M=K, Rb, Cs$, and Tl), and in $C2/m$ (12) there are seven sulfides ($M=Mg, Zn, Cd, Ag, Fe, Mn, Ni$). The structures of the mercury compounds are unique: $C2/c$ (15) for $Hg_2P_2Se_6$ and $P\bar{1}$ (1) for $Hg_2P_2S_6$.

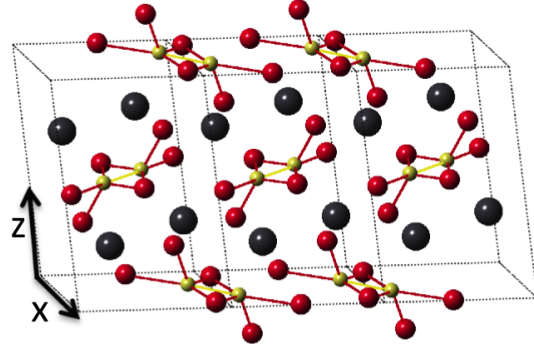


FIG. 4: The structure of $\text{Pb}_2\text{P}_2\text{Se}_6$ in monoclinic Pc symmetry has alternating layers of Pb ions (black) and P_2Se_6 . Each P (gold) is bound to four Se (red) in a distorted tetrahedral arrangement. Polarization arises from asymmetric displacements of Pb along the (101) direction.

In contrast, the number of entries with polar structures is much lower: in Pc (7) there are the four ferroelectric compounds, $\text{Sn}_2\text{P}_2(\text{S},\text{Se})_6$, $\text{Pb}_2\text{P}_2(\text{S},\text{Se})_6$, discussed above. $\text{K}_2\text{P}_2\text{Se}_6$ is reported in space group $P3_1$ (144), and $\text{Cd}_2\text{P}_2\text{S}_6$ and $\text{Fe}_2\text{P}_2\text{Se}_6$ in group $R3$ (146).

This list suggests three different avenues for investigating polar compounds and possible ferroelectricity in these systems. The first is to use first-principles calculations to investigate whether the selenides with $M = \text{Ca}, \text{Sr}, \text{Ba}$ and Eu might have ground state ferroelectric structures analogous to those of $M = \text{Sn}$ and Pb . This is not very promising, as the proposal that a lone pair is necessary to generate the asymmetric displacements needed for the polarization [78, 79] seems quite reasonable. Our list also contains two additional structure types that show indications of ferroelectricity. Thus, another avenue would be further to investigate the polar compound $\text{K}_2\text{P}_2\text{Se}_6$. Unfortunately, this structure is a polymeric helical crystal with over one hundred atoms per unit cell, and therefore is not well-suited for full first-principles investigation.

The third avenue is the most promising: to investigate the rhombohedral compounds that show indications of ferroelectricity, as the two $R3$ compounds $\text{Cd}_2\text{P}_2\text{S}_6$ and $\text{Fe}_2\text{P}_2\text{Se}_6$ have relatively simple structures. ISOTROPY analysis shows that space group 146 is related to the higher symmetry group 148 by a zone-center polar Γ_1^- mode. In the nonpolar $R\bar{3}$ (148) space group, in addition to a candidate paraelectric partner reported for the Fe compound, there are three additional compounds already listed above: the selenides with $M = \text{Mg}, \text{Zn}$, and Mn . These nonpolar phases have been well studied [80, 81]. Their structures are related to the CdI_2 structure type, which can be described as layers of edge-sharing Cd-centered halogen octahedra stacked in an AB order sequence.

The rhombohedral $R\bar{3}$ and $R3$ structures (Figure 5) reported for the $M_2\text{P}_2X_6$ entries are derived from the CdCl_2 structure by replacing the halogen with S or Se, occupying 2/3 of the octahedral sites with M and the remaining one-third by a diphosphorous unit aligned along the c direction [80]. The polar distortion in $R3$ is a Γ_1^- mode which consists of small displacements of the M and P_2 units along the c direction.

We used a first-principles approach with LSDA to investigate possible ferroelectricity in rhombohedral both $\text{Cd}_2\text{P}_2\text{S}_6$ and $\text{Fe}_2\text{P}_2\text{Se}_6$. With the reported $R3$ structures as the starting structure, we performed structural relaxations to find that the polar distortion disappears and the system relaxes to a nonpolar $R\bar{3}$ structure. While it might be that a more accurate treatment of electronic correlations, for example with $\text{DFT}+U$, is needed to capture the ferroelectric instability, from the present result we conclude that neither $\text{Fe}_2\text{P}_2\text{Se}_6$ or $\text{Cd}_2\text{P}_2\text{S}_6$ is ferroelectric. As in the case of $\text{Sr}(\text{Sb}_{1/2}\text{Mn}_{1/2})\text{O}_3$ discussed previously, this negative result is disappointing in the search for new ferroelectrics, but does illustrate the value of including first principles results in evaluating structural data.

While this investigation did not definitively identify any new ferroelectric compounds, the results suggest that it is a useful strategy to consider the variety of structure types exhibited by a simple compositional formula (in this case, 1:1:3 with P and either S or Se). As in this case, this approach could bring to light smaller structural families which have received less attention, but could have additional, as yet unknown, representatives with polar instabilities and desirable properties.

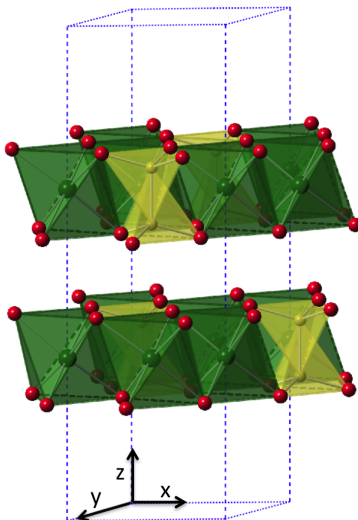


FIG. 5: The structure of $M_2P_2Se_6$ in hexagonal $R\bar{3}$ symmetry has 2/3 of the octahedral sites filled with M (green) and the remaining 1/3 filled with a P_2 unit (gold).

PROSPECTS

First principles predictions of structures and properties of real and hypothetical compounds are a powerful tool in the design of new materials with desirable properties [1, 2]. This power can be greatly amplified by integration of these methods, which address individual compounds one at a time, with database analysis, which permits a global view of the structure and stability of compounds and the relationships between compounds and classes of compounds [44, 82]. With recent increasing acceptance of this idea, it has become clear that there are many ways in which this integration can be achieved. In this paper, we have described how we have identified various strategies for this integration through three exploratory investigations searching for new ferroelectric semiconductors, in systems ranging from the familiar family of perovskite oxides with a main group element (Sb) sharing the B site with a transition metal (Mn) to promote a lower band gap, to the same combination of elements (Sb, Mn) in an edge-sharing octahedral structure, to chalcogenides based on P_2X_6 clusters. In this final section, we summarize the general strategies that have emerged from our work so far, and the main avenues we have identified for further investigation.

As a starting point, our survey of all polar systems in the ICSD allowed us to consider a very wide range of systems as candidate ferroelectrics. One result from the polar compound survey was the large number of orthorhombic polar compounds. This offers the exciting opportunity to perform a systematic investigation of these structures and, with the help of first principles results, to understand the underlying mechanisms that favor arrangement into polar structures, especially those which are related by small polar distortions to high-symmetry reference structures and thus are candidate ferroelectrics. The elucidation of one or more of these mechanisms would point the way to the design of related and perhaps radically new ferroelectric compounds.

One issue identified in our survey of the polar compounds is the need for better information about structure types. It would be very useful and quite practicable to introduce an automated classification of structure types within a given space group given occupied Wyckoff positions and structural parameters, making it easier to understand the structural information and to identify the relationships between compounds.

To screen the full collection of polar systems for systems with low band gap, we formulated a criterion that the system should include main group cations bound to either oxygen, sulfur or selenium. Our first investigation, described in Section 3.2, focused on a particular compound that satisfied both this chemical criterion and the structural criterion described above, and had in a previous database search [37] been identified as a candidate ferroelectric. Our initial purpose was to use first principles methods to more fully characterize the system, and in particular to obtain the band gap. However, it proved that the structure is in fact nonpolar, consistent with other reports in the literature. A similar conclusion was reached in the investigation of the reported polar $R\bar{3}$ chalcogenide $Fe_2P_2Se_6$ in Section 3.4. The lesson is that misassignment of nonpolar structures as polar does occur, and can be confirmed with the assistance of first principles results.

A complementary strategy emerged from the relationship of ferroelectrics to high-symmetry nonpolar reference structures, and the possibility that there might be many polar structures that have been misassigned as nonpolar in the database. Symmetry analysis tools such as ISOTROPY allow the easy identification of the relationships between different structure types in different space groups, particularly when the space groups have a group-subgroup relationship and the low symmetry structure is related by one or a few normal modes to the high-symmetry structure. While proper ferroelectrics, related to a high-symmetry reference structure by a zone-center polar mode, are often relatively easy to identify even without symmetry analysis software, this approach can also readily identify candidate improper ferroelectrics, in which the symmetry analysis is more subtle. We searched in particular for relatively low-symmetry nonpolar structure types as candidate high-symmetry reference structures. In addition to shifting the focus from the more familiar perovskites, this has the advantage that improper ferroelectricity is more likely to be found in relatively low symmetry nonpolar systems, in which a single nonpolar mode, which need not be at the zone center, can suffice to break the symmetry that forbids spontaneous polarization. For our second investigation, described in Section 3.3, we chose a particular system with a low-symmetry nonpolar structure, schafarzikite MSb_2O_4 , and checked for previously unrecognized instabilities of modes that would break the symmetry to a polar structure, both at the zone center and at other wave vectors as determined by symmetry analysis. Despite the lack of instabilities for this particular case, we believe that similar investigations of a wider range of systems will yield positive results. This suggests the usefulness of a complete compilation of a list of space groups and modes at high-symmetry wavevectors that break symmetry in such a way as to produce a polar space group.

The identification of polar instabilities in nonpolar reference structures could be facilitated by a complementary approach based on the first principles computation of full phonon dispersions. In order for a system to exhibit either proper or improper ferroelectricity, it is necessary that the relevant mode of the high-symmetry structure be unstable. The first principles computation of the phonon dispersion of a large number of nonpolar systems would allow screening of phonon instabilities or low-frequency (marginally stable) modes, leading to the identification of actual or incipient proper or improper ferroelectrics. More generally, the value of a systematic collection of first-principles phonon information has long been known for spectroscopic (IR/Raman) identification [83]. With respect to the misassignment of polar structures as nonpolar, or the identification of low-temperature transitions, systematic information about the phonon dispersions of nonpolar structures would establish how prevalent these might be, and assist in the development of principles to identify nonpolar structure types susceptible to polar instabilities.

Another strategy for the use of the database is to use a particular system of interest as a starting point and to survey compounds with the same structure, first to establish a pattern, and then to fill out the pattern to search for more and possibly better representatives. This was our initial purpose in Section 3.4, starting from $Sn_2P_2S_6$ and $Pb_2P_2S_6$, though in this case our search was unsuccessful. More generally, the capability of first principles calculations to compute the structure and stability of compounds lends itself naturally to high-throughput studies, in which a large number of compounds with a common formula and structure can be systematically searched for local stability, band gap, and functional properties such as elastic, dielectric and piezoelectric responses. Recent examples of such studies, discussed in the Introduction, include our own study of ferroelectricity and piezoelectricity in half-Heusler compounds [45]. As an outgrowth of that project, we subsequently considered the six common structure types with the same 1:1:1 formula, finding a class of previously overlooked ferroelectrics in the LiGaGe structure type (space group 186) and identifying individual examples in a high-throughput study [46]. This demonstrates the potential of this strategy in bringing to light structural families which have received less attention, but could have additional, as yet unknown, representatives with polar instabilities and desirable properties.

With increasingly powerful first principles approaches and with dramatic improvements in databases and in the synthetic capabilities needed to realize new materials in the laboratory, this is truly an exciting time for materials design. We eagerly look forward to rapid progress in this field and the successful discovery and design of new materials with fundamental scientific interest and valuable technological applications.

Acknowledgments

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